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Applicant(s): Yamanaka et al.

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For: **SYNTHETIC PAPER MADE OF STRETCHED POLYPROPYLENE FILM**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

FOURTH SUPPLEMENTAL DECLARATION

Sir:

I, Masaaki Yamanaka, do hereby declare:

1. I am one of the joint inventors of the present U.S. application;
2. I have been engaged in research and development of synthetic paper at Oji-Yuka Synthetic Paper Co., Ltd. since 1969;
3. I am an inventor of the following U.S. Patents: U.S. Patent Nos. 4,097,645, 4,340,639; 4,341,880; 4,418,112; 4,420,530; 4,472,227; 4,483,965; 4,663,216; 4,705,719; 4,795,676; 4,986,866; 5,254,302; 5,332,542; 5,409,754 and 5,670,225 and the corresponding foreign patents such as Japanese and European patents.
4. The experimentation outlined in the present U.S. application, the results thereof being documented on tables 1 and 2 therein; the experiments in the Declaration filed October 22, 1999 the results documented therein; the experiments in the Supplemental

Declaration filed April 9, 2001 the results documented therein; the experiments in the Second Supplemental Declaration filed August 5, 2002 the results documented therein; and the experiments in the Third Supplemental Declaration filed May 29, 2003 the results documented therein were carried out with my involvement, direction and supervision.

5. The following additional Experiments 1 and 2, the results presented in accompanying Tables 1-2, was also carried out with my involvement, direction and supervision and represents a "side-by-side" comparison of the claimed synthetic paper with one of Takashi et al. synthetic paper where the sole difference is the kind and amount of antistatic agent:

#### **EXPERIMENT 1**

1) Manufacture of a base layer (Composition (polypropylene: 80 parts by weight, polyamide: 20 parts by weight, diatomaceous earth: 0.5 part by weight, and dispersing agent: 0.1 part by weight) is based on the description in Table I (b) in the invention of Takashi et al.)

A duplicate experiment was made on Example 12 of U.S. Patent No. 4,318,950 (invention made by the parent company of Oji-Yuka Synthetic Paper Co., Ltd., which is one of the present assignees (This technique has been transferred to Oji-Yuka Synthetic Paper Co., Ltd.)).

A resin composition (A) comprising 80 parts by weight of NOVATEC PP MA-8 (polypropylene produced by Japan Polychem Corporation; melting point: 164°C), 20 parts by weight of polyamide (Nylon 6, UBE Nylon 1022 FDX23), manufactured by UBE Industries, Ltd., 0.5 parts by weight of diatomaceous earth, 0.1 parts by weight of NYMEEN S-210

(dispersant produced by NOF Corp.) was melt-kneaded through an extruder, and then extruded through a die into a sheet at a temperature of 250°C. The sheet thus formed was cooled to a temperature of about 50°C.

Subsequently, the sheet was heated to a temperature of about 145°C and this sheet was stretched by the machine 5 times using a peripheral velocity of rolls to obtain a machine-directionally stretched film. The machine-directional stretching conditions based on the description in Table III in the invention of Takashi et al. were used.

Separately, a resin composition (B) comprising 80 parts by weight of NOVATEC PP MA-8 (polypropylene produced by Japan Polychem Corporation; melting point: 165°C), 20 parts by weight of polyamide (UBE Nylon 1022FDX23 – manufactured by Engelhard Minerals & Chemicals Co.), 80 parts by weight of clay having a particle diameter of 1µm produced by ENGELHARD MINERALS & CHEMICALS CO., 0.7 parts by weight of low molecular weight antistatic agent (PHOSPHANOL RL-20<sup>1</sup>), 0.5 parts by weight of NYMEEN S-210 (dispersant produced by NOF Corp.) was separately melt-kneaded through two extruders, and then through a die to produce a film on both surfaces of the machine-directionally stretched base film and then laminated (B/A/B) to form a laminate (paper-like layer/base layer/paper-like layer).

The three-layer film (B/A/B) was introduced into a tenter oven where it was then heated to a temperature of 160°C. The film was then oriented crosswise by a factor of 7 at a temperature

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<sup>1</sup> Trade name has been changed from SM-1, manufactured by Toho Chemical Industry Co., Ltd because the low molecular weight antistatic agent "RE SISTAT PE 132" used in Ex. 12 of U.S Patent 4,318,950 has been discontinued and the low molecular weight antistatic agent used in Ex. 1 of U.S. Patent 4,318,950 was used instead.

of 140°C using the tenter. It is noted that the transverse directional stretching conditions are based on the description in Table III in the invention of Takashi et al. Subsequently, the stretched film was subjected to corona discharge treatment at 70 W/m<sup>2</sup>/min on the side of the paper-like layer (B layer), cooled to a temperature of 55°C, and trimmed. The thickness of the three-layer stretched film was 140µm and the thickness of the individual layer (B/A/B) of the three-layer stretched film was 140µm and the thickness of the individual layers (B/A/B) of the three-layer stretched film were 50µm/40µm/50µm (The thickness are based on the description in Table IV in the invention of Takashi et al.). The synthetic film thus obtained has a three-layer structure and is a composite film containing a biaxially oriented stretched base layer and two uniaxially oriented stretched paper-like layers (surface layers).

### **EXPERIMENT 2**

A three-layered composite film structure containing a biaxially-oriented stretched base layer and two uniaxially-oriented paper-like surface layers was prepared in the same manner as in Experiment 1 above, except instead of PHOSPHANOL RL-20, (produced by TOHO Chemical Inc.) was changed to a high-molecular weight antistatic agent (polyethersteramide used in Example 1 of the present invention. The results are set forth in tables 1 and 2 and further discussed after the description of experiment 4.

### **EXPERIMENT 3**

A three-layered composite film structure containing a biaxially-oriented stretched base layer and two uniaxially-oriented paper-like surface layers was prepared in the same manner as in Experiment 1 above, except instead of using the low molecular weight antistatic agent at 0.7

parts by weight, 20 parts by weight was used. In addition, after laminating the paper-like layer to the base layer, the low molecular weight antistatic agent was bled out from the paper-like layer and the surface tackiness was generated on a forming roll.

It was noted that the antistatic agent that bled out of the paper-like layer causing tackiness on the forming roll was very difficult to handle. In fact the handling was so difficult that the synthetic paper could not be manufactured.

As with Experiment 2, the results are set forth in tables 1 and 2 and are discussed after the description of Experiment 4.

#### **EXPERIMENT 4**

A three-layered composite film structure containing a biaxially-oriented stretched base layer and two-uniaxially oriented paper-like surface layers was prepared as in Example 1 of the present invention. The procedure directly follows and the results are discussed below:

(1) Into a mixture of 80 wt% polypropylene having an MFR of 0.8 g/10 min, a melting point of 164°C (DSC peak temperature), and a degree of crystallinity of 67% (manufactured by Mitsubishi Chemical Corp.) and 8 wt% high-density polyethylene (manufactured by Mitsubishi Chemical Corp.) was incorporated 12 wt % calcium carbonate having an average particle diameter of 1.5  $\mu\text{m}$ . The resulting composition (I) was melt-kneaded with an extruder set at 270°C, subsequently extruded into a film, and then cooled with a cooler to obtain an unstretched film. After being heated to 140°C, this film was stretched in the machine direction 5 times.

(2) Using a Henschel mixer, 54 wt % polyetherester-amide [B1] obtained in Production Example 1 was mixed for 3 minutes with 18 wt % polyamide resin (UBE Nylon 1013B manufactured by UBE Industries, Inc.), 18 wt % acid-modified low-molecular weight polypropylene having an MFR of 4 g/10 min (manufactured by Mitsubishi Chemical Corp.). The resulting mixture was kneaded with a vented twin-screw extruder set at 240°C, extruded into strands with a die, and then cut to obtain a master batch [M] in a pellet form.

(3) Polypropylene having an MFR of 4 g/10 min, a melting point of 164°C, and a degree of crystallinity of 64% (manufactured by Mitsubishi Chemical Corp.) was mixed in an amount of 38 wt% with 40 wt% calcium carbonate having an average particle diameter of 0.8µm, and 17 wt % master batch [M], containing a permanent antistatic agent and obtained in (2) above. The resulting composition (III) was melt-kneaded with an extruder and then stretched film having a stretching ratio of 5 obtained in (1) above.

This three-layer laminate was heated to 155°C, and then stretched in the transverse direction 8 times with a tenter-stretching machine to obtain a stretched film. Subsequently, the stretched film was treated with 50 W/m<sup>2</sup> min corona discharge using a discharge device manufactured by Kasuga Denki Co., Ltd. to obtain a three-layer stretched film.

The thickness of the individual layers ( (III)/(I)/(II) ) of this three-layer stretched film was 20 µm/60 µm/20 µm.

## **Results**

The resulting papers produced in Experiments 1-4 were evaluated according to the

evaluation methods of synthetic papers of the present invention. Namely, (1) surface resistivities of the synthetic papers resulting from each experiment were evaluated before and after washing with water and the results are set forth in Table 1 attached herewith. Also evaluated was (2) ink adhesion and suitable for paper feeding/discharge as the offset printability were also evaluated. The results are set forth in Table 2 attached herewith.

### Surface Resistivity ( $\Omega$ )

Experiment 1: The surface resistivity of the synthetic paper containing 0.7 parts by weight of low molecular weight antistatic agent as in Experiment 1 was  $2 \times 10^{13} \Omega$  before washing with water and  $1 \times 10^{10} \Omega$  after washing with water. The surface resistivity before washing was somewhat unproned but deteriorated after it was washed with water. This was because the low molecular weight antistatic agent on the surface of the synthetic paper was washed out

Experiment 2: The surface resistivity of the synthetic paper containing 0.7 parts by weight of high molecular weight antistatic agent was measured at  $2 \times 10^{14} \Omega$  before washing and  $2 \times 10^{14} \Omega$  after washing. Thus, the surface resistivity of the synthetic paper of Experiment 2 did not change indicating that the high molecular antistatic agent was not washed off in water.

Experiment 3: The surface resistivity of the synthetic paper prepared according to the procedure of Experiment 3 was  $1 \times 10^{18} \Omega$  before washing with water, which was somewhat unproned, but was  $5 \times 10^{15} \Omega$  after washing with water indicating at least part of the low molecular weight antistatic agent was washed out.

Experiment 4: Finally, the surface resistivity produced according to procedure of Experiment 4 was  $4 \times 10^{11} \Omega$  before washing with water and was  $3 \times 10^{11} \Omega$  after washing with water. Thus, indicating that the amount of antistatic agent wash off was very minimal, if any.

#### Offset Printability (Ink Adhesion)

Experiment 1: The ink adhesion of the synthetic paper produced according to Experiment 1 was evaluated as "Δ", which was a level to become at least partially problematic. The suitability for paper feeding/discharge was evaluated and reported in table 2. An "x" in table 2 indicates that the paper was not suitable and would probably cause a high frequency of paper feeding/discharge trouble.

Experiment 2: Evaluation of the ink adhesion on the synthetic paper of Experiment 2 was indicated as "Δ" in table 2, which was a level to become practically problematic. As with the product produced in Experiment 1, the experiment 2 product also would probably cause a high frequency of feeding/discharge trouble as indicated in Table 2.

Experiment 3: Evaluation of the ink adhesion on the synthetic paper of Experiment 3 was also "Δ" at a level that would become practically problematic. As with Experiments 1 and 2 the "x" rating in Table 2 indicates because of high resistivity, which was a level to become problematic because of high frequency of paper feeding/discharge trouble.



Experiment 4: Unlike the synthetic papers produced according to Experiments 1-3, the synthetic paper produced according to Experiment 4 had favorable evaluations, as indicated by “Ⓢ” in Table 2, for both ink adhesion on the synthetic paper and for paper feeding /discharge. In other words, the ink adhesion on the synthetic paper produced according the experiment 4 would NOT become practically problematic and there would not be a high frequency of paper feeding/discharge trouble because of a high surface resistivity. Thus, the synthetic paper of Experiments 1-3 are practically unacceptable, where the synthetic paper of experiment 4, which was produced according to Example 1 of the present application, is far more superior and therefore is practically acceptable for the market.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

July 31, 2006  
Date

Masaaki Yamanaka  
Masaaki Yamanaka

**Table 1**

<b>Components: Paper-like Layer</b>								
	<b>Resin</b>	<b>Parts</b>	<b>Filler</b>	<b>Parts</b>	<b>Anti-static Agent</b>	<b>Parts</b>	<b>Dispersing Agent</b>	<b>Parts</b>
<b>Ex. 1</b>	PP**	80	clay	80	PHOSPANOL SM-1	0.7	NYMEEN S-210	0.5
	Polyamide	20						
<b>Ex. 2</b>	PP**	80	clay	80	PEEA	0.7	NYMEEN S-210	0.5
	Polyamide	20						
<b>Ex. 3</b>	PP**	80	clay	80	PHOSPANOL SM-1	20	NYMEEN S-210	0.5
	Polyamide	20						
<b>Ex. 4</b>	PP**	72.3	CaCO <sub>3</sub>	72.7	PEEA	16.7		
	Polyamide	5.5	TiO <sub>2</sub>	9.1				
	Modified PP	5.5						
<b>Components: Base Layer</b>								
	<b>Resin</b>	<b>Parts</b>	<b>Filler</b>	<b>Parts</b>	<b>Anti-static Agent</b>	<b>Parts</b>	<b>Dispersing Agent</b>	<b>Parts</b>
<b>Ex. 1</b>	PP**	80	Kiesel-	0.5			NYMEEN S-210	0.1
	Polyamide	20	Guhr					
<b>Ex. 2</b>	PP**	80	Kiesel-	0.5			NYMEEN S-210	0.1
	Polyamide	20	Guhr					
<b>Ex. 3</b>	PP**	80	Kiesel-	0.5			NYMEEN S-210	0.1
	Polyamide	20	Guhr					
<b>Ex. 4</b>	PP**	80	CaCO <sub>3</sub>	12				
	PE	8						

\*\*1: (In Exs. 1 to 3, the amounts of the components are expressed in terms of parts by weight)

\*\*2: (In Ex. 4, the amounts of the resins added (inclusive of PEEA) are expressed in terms of % by weight.)

\*\*3: (In Ex. 4, the amounts of the fillers added are expressed in terms of parts by weight based on 100 parts by weight of resins inclusive of PEEA.)

\*\*4: (In Ex. 4, the amounts of the components added are expressed in terms of % by weight)

PP\*1: Polypropylene, "Novatec PP, MA-8" (trade name), manufactured by Japan Polypropylene Corporation  
PP\*2: Polypropylene, "Novatec PP, MA-3" (trade name), manufactured by Japan Polypropylene Corporation  
Polyamide: Nylon 6, "UBE Nylon 1022FDX23" (trade name), manufactured by Ube Industries, Ltd.

PE: Polyethylene, "Novatec IID, HJ580" (trade name), manufactured by Japan Polyethylene Corporation

CaCO<sub>3</sub>: "Softon 1800" (trade name), manufactured by Shiraishi Calcium Kaisha Ltd.

TiO<sub>2</sub>: "CR-60" (trade name), manufactured by Ishihara Sangyo Co., Ltd.

PHOSPHANOL SM-1: "PHOSPHANOL RL-210" (trade name has been changed), manufactured by Toho chemical Industry Co., Ltd.

NYMEENS-210: manufactured by NOF Corporation

PEEA: polyetheresteramide of Production Example 1 of the present application

Modified PP: Acid-modified polypropylene of Production Example 3 of the present application

**Table 2**

	Stretching/Surface Treatment				Evaluation			
	Thickness ( $\mu\text{m}$ )	Stretching of paper-like layer		Surface Treatment	Surface resistivity ( $\Omega$ )		Offset printability	
	Front/core/back	Stretching	Stretching ratio		(a)	(b)	Ink adhesion	Suitability for paper feeding/discharge
Ex. 1	50/40/50	uniaxial	7	Corona	$2 \times 10^{13}$	$1 \times 10^{16}$	$\Delta$	x
Ex. 2	50/40/50	uniaxial	7	Corona	$2 \times 10^{13}$	$2 \times 10^{16}$	$\Delta$	x
Ex. 3	50/40/50	uniaxial	7	Corona	$1 \times 10^{13}$	$5 \times 10^{16}$	$\Delta$	x
Ex. 4	20/50/20	uniaxial	8	Corona	$4 \times 10^{11}$	$3 \times 10^{11}$	$\odot$	$\odot$

\*\*\*1

\*\*\*2

\*\*\*1: Before washing with water

\*\*\*2: After washing with water